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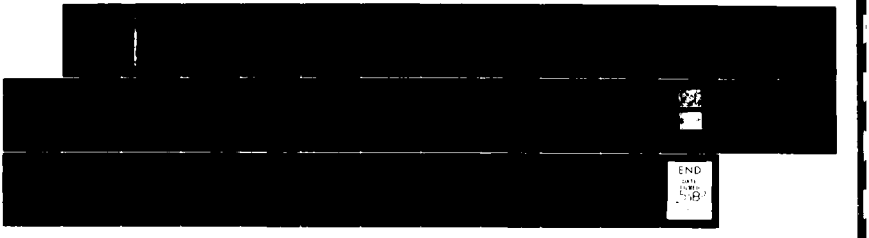

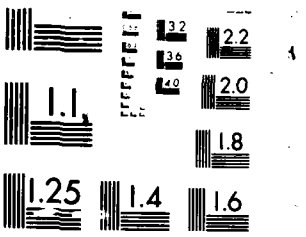

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REPORT

MRL-R-1037

THE KINETICS AND THERMOCHEMISTRY OF THE PYROTECHNIC COMPOSITION BLC-190 - BORON:RED LEAD OXIDE (10:90) AT ITS IGNITION TEMPERATURE

D.J. Whelan, M. Maksacheff
and L. de Yong

Approved for Public Release

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The thermal decomposition of the important pyrotechnic composition BLC 190 (boron:red lead, 10:90) has been studied by isothermal and non-isothermal differential scanning calorimetry (aluminium sample pans, nitrogen atmosphere). The decomposition has been found to proceed at temperatures around 700 K through a first-order reaction obeying a simple Arrhenius law with an activation energy 434 kJ/mol^{-1}, pre-exponential $\log_{10}A/(s^{-1})$ = 29.7 and heat of reaction 846 J/g^{-1}.

No change in weight was observed in the reaction mixture, before and after heating and the end-product is a lead borate salt, $PbO.2B_2O_3$ or PbB_4O_7, rather than boric oxide. The reaction pathway appears to have a kinetic step similar to that of BPBO (boron: PbO, 10:90).

(Keywords: pyrotechnics, lead compounds, boron compounds)

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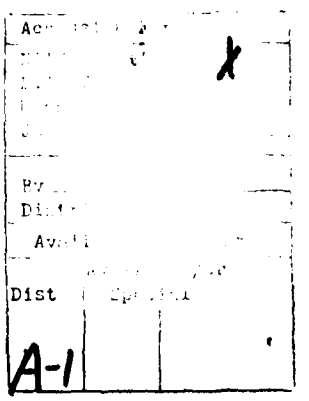

THE KINETICS AND THERMOCHEMISTRY OF THE PYROTECHNIC COMPOSITION BLC 190 - BORON:RED LEAD OXIDE (10:90) - AT ITS IGNITION TEMPERATURE

1. INTRODUCTION

In 1980, Bentley and Elischer [1] developed a new gasless pyrotechnic composition for use in percussion caps. This composition was tested in M42 cup assemblies [1,2] and was found to have a sensitivity comparable to those of gassy compositions currently used in those caps in service, as well as having a thermal output sufficient (but undefined) to ignite pyrotechnic delay units reliably. The pyrotechnic component of this composition consisted of boron (10 per cent, by weight) and red lead Pb_3O_4 (90 per cent, by weight), a formulation the present authors have designated BLC 190. The sensitivity of BLC 190 to stab- and to percussion-initiation was enhanced by the incorporation of a small amount (2 to 5 per cent) of the primary explosive, tetrazene [1].

This paper reports on the kinetics and thermochemistry of BLC 190, as studied by isothermal and non-isothermal differential scanning calorimetry (DSC). The temperature of ignition of BLC 190 (as measured on unconfined 50 mg samples, in air heated at $5^{\circ}C\ min^{-1}$) had been previously determined to be ca. 683 K (uncorr.) [3]. In the present instance, it was found that the low-temperature thermal decomposition of BLC 190 (aluminium sample pans) proceeds at about 690 K in the differential scanning calorimeter (DSC) under nitrogen and it follows a first-order reaction which obeys a simple Arrhenius law.

2. EXPERIMENTAL

2.1 Materials

The sample of boron used in this investigation was a washed technical grade material (ex Trona, American Potash Corporation), nominal average particle size 0.5–2.0 micron [4]. Particle sizing measurements carried out on the Malvern Particle Size Analyser indicated that the average particle size was "sub-micron", a result confirmed by scanning electron microscopy (Fig. 1) [5].

The non-isothermal DSC trace of this material (at a heating rate of 5 K min^{-1}) consisted of three endotherms, extending from 355 K to 450 K (Fig. 2). The origin of these endotherms was not investigated except that it is worth noting that, in compositions containing only 10 per cent boron, the magnitude of these endotherms would probably be insignificant. It is widely recognised that commercial grade boron is ca. 85–95 per cent pure, the suggested main impurities being moisture, sub-oxides of boron and/or magnesium borides [4,6]. Analyses of the sample of boron used in the formulation BLC 190 gave its magnesium content as 6% (atomic emission spectroscopy) and total boron content as 91% (wet-way analysis) [7].

Red lead, Pb_3O_4, was an analytical grade reagent, supplied by May and Baker. It was reported to assay at 85 per cent (minimum) Pb_3O_4, the residue being PbO (< 15 per cent), the by-product of the method of manufacture [6]. Subsequent analysis using powdered x-ray diffraction techniques confirmed this assay, the sample being identified as Pb_3O_4 ("minium") containing 6.0 per cent PbO ("massicot") [5]. The nominal particle size of the material was determined to be ca. 6 micron (weight basis), the histogram of particle size distribution being reproduced in Fig. 3.

The DSC trace from Pb_3O_4 over the temperature range 350 K to 870 K is very similar to that reported by Al-Kazraji and Rees [8]. At a heating rate of 5 K min^{-1}, there is observed a weak endotherm between 550 K and 610 K and a relatively weak exotherm between ca. 735 K and 821 K (Fig. 4).

The change in weight associated with these processes corresponded to a weight loss of 2.3 per cent based on Pb_3O_4 (ca. 10 mg) – consistent with the following reaction occurring under nitrogen:

$$2\ Pb_3O_4 \rightarrow 6\ PbO + O_2,$$

a reaction which has been reported to occur around 800 K, with a net uptake of heat [8] and theoretical weight loss of 2.33 per cent.

In the present instance, a net evolution of heat was observed and one may ask if this is due to additional reaction occurring between a reactive intermediate (Pb_3O_4 or PbO at high temperature) with the aluminium sample pan,

the reaction being accompanied by liberation of O_2. This deserves to be investigated further.

The pyrotechnic composition was prepared in a standard way by repetitive dry mix - sieving to produce a homogeneous blend of the ingredients.

2.2 Differential Scanning Calorimetry

Thermochemical measurements were obtained using a Perkin-Elmer DSC-2C Differential Scanning Calorimeter operating in either the isothermal or non-isothermal mode as required and controlled by a Perkin-Elmer Model 3600 Data Station with appropriate software.

All samples were accurately weighed on a Mettler ME30 Microanalytical Balance directly into aluminium sample pans and lids placed (but not crimped) over the samples [9].

The sample and reference compartments of the calorimeter were continuously purged with nitrogen gas throughout the DSC scans, the nitrogen flow rate typically being 20-25 ml min^{-1}.

Temperature calibration was carried out using NBS thermal analysis standards, indium (m.p. 429.8 K, heat of fusion 28.6 J g^{-1} [10,11]) and zinc (m.p. 792.7 K [10]).

Samples of BLC 190 were weighed on the microbalance before and after each DSC run. No change in mass was observed as a result of the reaction process.

3. RESULTS

3.1 Non-isothermal DSC Traces from BLC 190

The DSC trace from BLC 190 near 700 K consists of a single sharp exotherm, whose "peak temperature" or "temperature at which the rate of dissipation of heat is greatest" and "onset temperature" depend on the rate of heating of the sample (Table 1). The area under the DSC trace measures the heat of reaction of the process under investigation and is, in this case, independent of heating rate.

In the DSC experiment carried out at a heating rate of 5 K min^{-1} (the heating rate corresponding to the conventional "temperature of ignition"

experiments), it can be seen (Fig. 5) that thermal decomposition commences near 678 K and that the (extrapolated) onset temperature for the reaction exotherm occurs at 694 K; a maximum heat output occurs at 714 K. These results compare with a temperature of ignition of BLC 190, as measured on the conventional T of I apparatus [3] and quoted in the Introduction, of 683 K (uncorr.).

At a heating rate of 20 K min^{-1}, the "onset" and "peak" temperatures occur at 707 K and 728 K respectively (Fig. 6).

The kinetic parameters of the thermal decomposition of BLC 190, namely E*, the activation energy, the (apparent) first-order Arrhenius pre-exponential term, A, and the reaction order, n, were determined from treatment of DSC data described by Kissinger [12,13], Hauser and Field [14], and Dollimore and co-workers [15].

In this approach, Kissinger [12] established that there is a relationship between the peak temperature (T_m) and the heating rate for an (apparent) first-order reaction and this relationship can be summarized by the equation

$$A \exp(-E^*/RT) = \frac{E^*}{RT_m^2} \cdot \frac{dT}{dt} \qquad (1)$$

where R is the gas constant, T_m is the peak temperature and dT/dt is the time rate of heating of the sample. This can be written as

$$\ln \frac{\phi}{T_m^2} = \ln \left(\frac{RA}{E^*}\right) - \frac{E^*}{R} \cdot \frac{1}{T_m} \qquad (2)$$

where $\phi = dT/dt$, from which a plot of $\ln(\phi/T_m^2)$ vs. $1/T_m$ is a straight line, slope $-E^*/R$.

Kissinger showed that, even for an n th-order reaction, reasonable approximations can be made which reduce the kinetics to a form where this equation can apply, regardless of reaction order; the pre-exponential term, A, has the dimensions $(time)^{-1}$ and can be regarded as a pseudo first-order constant [13].

When the data in Table 1 was plotted out according to equation (2), the following parameters were obtained,

$$E^* = 420.4 \text{ kJ mole}^{-1},$$
$$\log_{10} A\ (s^{-1}) = 28.66$$

the correlation coefficient of the plot being 0.9948.

From a line shape analysis of the DSC traces at the four different heating rates, the order of reaction was determined to be first-order ($n = 0.99 \pm 0.03$) [13] and the heat of reaction determined as 820 ± 29 J g^{-1} (196 ± 7 cal.g^{-1}, from 10 experiments). These results are incorporated within Table 1.

Analysis of these non-isothermal DSC traces using the Perkin Elmer software package "KINETICS" [16] was unsatisfactory (Table 2). While the approach described in the software manual appeared reasonable, it can be seen that the values determined for the Arrhenius pre-exponential factor, the activation energy and the reaction order all depend very much on the cut-off temperatures over which the analysis is made. Several DSC traces were analysed using this approach and the results were all equally disappointing.

3.2 Isothermal DSC Traces from BLC 190

Isothermal DSC traces were carried out following the procedure described in the Perkin Elmer Software Package "ISOTHERMAL" using thermally-balanced sample and reference compartments [17]. From non-isothermal DSC traces, it was apparent that BLC 190 was quite stable at temperatures below 650 K and that slow but obvious decomposition appeared to occur only above ca. 675-680 K.

Preliminary experiments suggested that the progress of the reaction could be conveniently followed by DSC studies over the "nominal" temperature range 690-705 K.

Accordingly, in a typical experiment, the sample (in an aluminium sample pan) was loaded into the sample compartment of the calorimeter, which had been previously heated to a temperature of 80 K below the temperature chosen for the study. The sample was allowed to equilibrate at this temperature (ca. two minutes) and then the temperature of the calorimeter raised rapidly (at 80 K min^{-1}) to the final temperature. The progress of the reaction was followed by observing the change in output of heat (dQ/dt) with time (t).

A typical isothermal thermogram for a run carried out at 705 K is given in Fig. 7 - the output being "corrected" for the output associated with "blank runs" at 705 K. In Figure 8, the same data is reproduced in an alternative form, viz. heat output vs. time.

From an analysis of the data presented in Fig. 7, one obtains the amount of fractional decomposition, α, at any time, t, by dividing the area under the curve from t=0 to t by the total area under the curve (which is a measure of the heat of reaction of the overall process).

The curve follows the first order rate law

$$\frac{d}{dt}\alpha = k_1 (1 - \alpha) \qquad (3)$$

(with $k_1 = 0.172 \pm 0.010$ min^{-1} at 705 K)

from a period 1.3 minutes after the commencement of the experiment, right through to a period of 22 minutes (5.5 half-lives or 97.7 per cent reaction). It has been suggested that the initial period (1.3 min., 78 sec.) recorded over the DSC run is typical of the time taken for the system to come to thermal equilibrium under the conditions of this experiment.

At 690 K, less than 3.5 per cent of the reaction occurred in this supposedly pre-thermal equilibrium stage and the reaction then followed first-order kinetics for greater than 94 per cent reaction (4.2 half-lives).

Whether this initial stage of the reaction is really due to "thermal lag" or not is debatable. It is possible that this period is also associated with "pre-steady state reaction" conditions where the reactants, Pb_3O_4 and boron, interact across their crystal boundaries, forming reactive centres or nuclei from which the pyrotechnic reaction ultimately proceeds [18,19], in this case following first-order kinetics.

Runs carried out at "nominal" temperatures of 690 K, 695 K, 700 K and 705 K, after a short pre-thermal equilibrium stage, all followed first-order kinetics, as described by eq. 3. The calculated first-order rate constants are given in Table 3.

An Arrhenius plot, ln k vs. T^{-1}, of these data conformed to a straight line (Fig. 9), from which one can deduce

$$E^* = 448.7 \text{ kJ mole}^{-1},$$

$$\log_{10} A\ (s^{-1}) = 30.68.$$

The linearity of this Arrhenius plot from which these parameters were determined, however, is much better than the correlation coefficient (0.915) indicates; in the determination of the correlation coefficient, calculations were based on the "nominal value" of the abscissa (T^{-1}), no weight being given to the effect of the error-bars on this variable (see Appendix).

From the area under the isothermal DSC traces, the heat of reaction was found to be 872 ± 63 J g^{-1} (208 ± 15 cal g^{-1}).

These results are very similar to those from non-isothermal DSC reported above, indicating that, under both sets of conditions, one is observing the same reaction.

3.3 Comparison of Results

Processing the experimental data from the non-isothermal and from the isothermal DSC traces leads to very similar values for the Arrhenius parameters, for the reaction order, n, and for the heat of reaction associated with the thermal decomposition of BLC 190 under ignition conditions (Table 4). It also confirms the tacit assumption that the same reaction is being investigated over the temperature range employed for the two sets of experiments.

In future discussions, the averaged value of E*, A(s^{-1}), n and heat of reaction will be quoted, viz.

$E^* = 434$ kJ $mole^{-1}$

$\log_{10} A\ (s^{-1}) = 29.7$

$n = 1$

heat of reaction $= 846 \pm 46$ J g^{-1}.

Recently, there has been quite valid criticism of the practice of deducing kinetic functions from non-isothermal DSC methods [20]. In the present instance, the authors are satisfied that this criticism does not apply; the reaction order is "simple" and the results from the two approaches "consistent". This implies that the reaction of BLC 190 near 700 K appears to be kinetically single-staged and the reactants (presumably in the solid state) interact uniformly [19].

4. DISCUSSION

4.1 The Chemistry of BLC 190

In the study such as this, one is entitled to ask:

"What is the chemical reaction taking place in this system?"

and

"What is the significance of the kinetic data?"

The study being reported here is that of an exothermic solid-state reaction between Pb_3O_4 and B, the reactants being described thus:

	B	Pb_3O_4
Formula weight	10.8	685.6
% by weight of reagent	10	90
Nominal purity	ca. 91%	94%
Possible impurities	"Mg" (ca. 6%)	PbO (6%)
Particle size (weight basis)	submicron	6 μ (Fig. 3)
Rel. molec. stoichiometry	ca. 0.84	ca. 0.12

It is apparent that the "boron" is present in considerable excess.

It may be for this reason that the observed reaction

$$B + Pb_3O_4 \rightarrow \text{Products} + \text{Heat}$$

appears to proceed by first-order kinetics. Alternatively, the first order dependence may be attributed to a simple, but as yet unidentified, unimolecular reaction which is rate-determining.

The stoichiometry of the reaction has not been studied in this investigation, save that it has been observed that there is no "loss of mass" from the reaction pans during the decomposition process.

In their original publication, Bentley and Elischer [1] reported that maximum thermal output for their delay composition occurred in mixtures containing 8-12 per cent B. This is an interesting result but it was one based on end-use practicalities rather than chemical considerations.

As to the products from this reaction, it had been tacitly assumed at the outset of this investigation that the products from the thermal decomposition of BLC 190 near 700 K would be B_2O_3 and PbO - Pb.

However, the infra-red absorption spectrum (KBr disc) of the reaction products showed no evidence for the presence of boron oxides as such but showed broad bands at 1350 (s), 950 (s) and 650 (m) cm^{-1} (Fig. 10) which are apparently characteristic of borate salts [21,22].

To investigate this further, lead diborate ($PbO.2B_2O_3$) or (PbB_4O_7) was synthesised from stoichiometric amounts of PbO (or Pb_3O_4) and H_3BO_3 at 900-500°C (Pt crucible) [23,24]. Its infra-red spectrum (KBr disc), reproduced in Fig. 11, was found to have bands centered about 1380 (s), 950 (b), and 650 (m) cm^{-1}. This result supports the suggestion that the reaction products from BLC 190 at around 700 K are salts based on lead borate.

Confirmatory evidence could be obtained from Pb^{207}- and B^{11}- n.m.r. studies [25].

4.2 The Kinetic Data Relating to BLC 190

The kinetic data relating to BLC 190 are summarized in Table 4.

In a related study, the authors have made a preliminary report on the system, BPBO, B - PbO (10:90) in which the thermograms were much more complicated (see Fig. 12) than those from BLC 190. In BPBO [26], the DSC profiles were characterised by a pre-ignition exotherm (probably due to diffusion of B into the PbO lattice [27]) and two overlapping ignition exotherms, labelled "Q" and "R" in the original paper.

Analysis of these ignition exotherms is not unequivocal but they are resolvable (Table 5) and it is apparent that the Arrhenius parameters calculated for the lower temperature exotherm, "Q", viz.

$$E^* = 435 \text{ kJ mole}^{-1}, \log_{10} A\ (s^{-1}) = 30.25$$

Correlation Coefficient 0.982

are very similar (if not identical within experimental and theoretical uncertainties) to those of BLC 190. It is tempting, therefore, to suggest that the exotherm from BLC 190 and that of "Q" from BPBO arise from the same mechanistic process (possibly proceeding from the products of the catalytic decomposition of Pb_3O_4 to PbO or from PbO itself).

That the kinetic model followed by BLC 190 has turned out so simply was surprising. In a recently published study on the effect of particle size on the kinetics of reaction between MgO and Al_2O_3, Beretka and Brown [28] found that the kinetics of spinel formation, described by the equation

$$MgO + Al_2O_3 \rightarrow Mg\ Al_2O_4,$$

depend on the particle size of reactants. For small-sized (micron) reactants, the reaction follows a rate law consistent with Avrami-Erofeev nucleation kinetics with a plot of

$$\ln \ln (1 - \alpha)^{-1} \text{ vs. } \ln t$$

being linear. For larger-sized reactants (45-55 micron), far less complicated linear first-order kinetics were followed.

It is quite possible that a similar trend could be occurring in the BLC 190 system, the practical result being that the effect of changes in performance may be able to be predicted from kinetic studies using DSC techniques.

5. CONCLUSIONS

The low-temperature thermal decomposition of BLC 190 near its ignition temperature in an inert atmosphere (Al sample pans) proceeds through a simple first-order reaction in the DSC calorimeter. The Arrhenius parameters describing this reaction are

$$E^* = 434 \text{ kJ mole}^{-1}$$

$$\log_{10} A\ (s^{-1}) = 29.67$$

with a heat of reaction of 846 J g^{-1}.

There is no weight change in the reaction and it appears as if the overall reaction corresponds to oxidation of boron with the formation of borate.

As far as the authors can ascertain, this study is one of the very few which has attempted to analyse kinetic data by the Kissinger method (using non-isothermal DSC) and reconcile it successfully with isothermal kinetic studies.

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APPENDIX

The Effect of Temperature Variations on Isothermal Rate Constants

It is widely recognised that the temperature dependence of most chemical reactions follows the Arrhenius equation,

$$k' = A \exp(-E^*/RT) \qquad (A1)$$

provided that the temperature range is not large.

Assuming A and E do not change, it can be shown quite simply that

$$\frac{\delta k'}{k'} = \frac{E^*}{RT^2} \delta T \qquad (A2)$$

For BLC 190, the activation energy, E*, was found to be 448.7 kJ $mole^{-1}$. Therefore, at 695 K, eq. A2 reduced to

$$\frac{\delta k'}{k'} = 0.113 \, \delta T \qquad (A3)$$

This means that, for an error in T of 1 K, the observed rate constant would change by 11 per cent at 695 K (nominal).

In the experiments described here, the temperature recorded on the panel of the DSC calorimeter was checked regularly (zinc standard). The deviation in temperature calibration over the course of runs at a particular nominal temperature varied from ± 0.5 K for reactions at 705 K to ± 2.5 K for reactions at 690 K.

The authors believe that, for a particular run, the reaction proceeds under isothermal conditions but the value of the actual temperature assigned to particular runs at a fixed nominal temperature may vary from run to run. Hence the apparently low correlation coefficient (Table 3).

TABLE 1

Non-isothermal DSC Characteristics of the Exotherm associated with the Thermal Decomposition of BLC 190

Heating Rate ($K\ min^{-1}$)	Mass of Samples (mg)	Exotherm T_{onset} (K)	Exotherm T_{max} (K)
20	3.05, 2.96	707.4	728.2
10	3.12, 3.09	699.5	720.2
5	3.10, 3.17	694.1	713.8
2.5	3.22, 3.24	690.0	707.6

Heat of Reaction 820 ± 29 J g^{-1} (196 ± 7 cal g^{-1})

Kissinger Plot

Activation energy, E* ($kJ\ mole^{-1}$)	420.4 ± 21
Pre-exponential $\log_{10}A$ (sec^{-1})	28.66 ± 0.87
Reaction Order	0.992 ± 0.031
Correlation Coefficient	0.995

TABLE 2

Kinetic Analysis of Non-Isothermal DSC Trace of BLC 190
using Perkin Elmer Software Package "KINETICS"

Reference Trace:	PTA 03.9A (31 January 1985)
Sample:	BLC 190, 2.96 mg
Heating Rate:	20 K min^{-1}
Reference:	Figure 6, this report
Heat of Reaction:	202.5 cal g^{-1} (847 J g^{-1})
Peak Range:	685 K - 774 K

Kinetic Analysis		Calculated Kinetic Parameters		
from T(K)	to T(K)	$\log_{10}A$ (s^{-1})	E* (kJ $mole^{-1}$)	Order
706.9	743.7	54.24 ± 1.2	752 ± 16	2.10
709.8	739.7	50.93 ± 1.1	708 ± 15	1.89
715.4	735.2	45.04 ± 1.0	630 ± 14	1.54
720.0	732.0	40.20 ± 0.9	565 ± 12	1.29
724.5	730.0	28.44 ± 0.6	408 ± 8	0.90
Comparison				
Kissinger Plot		28.66 ± 0.9	420 ± 21	0.99
Isothermal Data		30.68	449	1

TABLE 3

Kinetics of Thermal Decomposition of BLC 190 as studied by isothermal DSC between 690 K and 705 K

Temperature (nominal)	Temperature (actual)	First Order Rate Constant (k_1, min^{-1})	First Order Half-Life (min)
690	690 ± 2.5	0.0378	18.3
690		0.0212	32.7
695	695 ± 0.8	0.0709	9.8
695		0.0594	11.7
700	700 ± 0.4	0.0830	8.3
700		0.0903	7.7
705	705 ± 0.5	0.1720	4.0
705		0.1550	4.5

Masses of samples typically 2.2 - 2.7 mg

Heat of reaction, 872 ± 63 J g^{-1} (208 ± 15 cal g^{-1})

Arrhenius Plot

Activation energy, E* (kJ $mole^{-1}$)	448.7
Preexponential $\log_{10}A$ (s^{-1})	30.68
Reaction Order	First
Correlation Coefficient	0.915

TABLE 4

Comparison of the Kinetic Data from Isothermal and Non-isothermal DSC Studies on the Thermal Decomposition of BLC 190 near its Temperature of Ignition

	Non-Isothermal (Kissinger)	Isothermal (Arrhenius)	Average
E^* (kJ mole^{-1})	420 ± 21	449	434
$\log_{10}A$ (s^{-1})	28.66 ± 0.87	30.68	29.7
Correlation Coefficient	0.995	0.915	-
Reaction Order	0.99 ± 0.03	1	1
Heat of Reaction (J g^{-1})	820 ± 29	872 ± 53	846 ± 46

Compare: BPBO, Exotherm "Q"

E^* = 435.4 kJ mole^{-1}

$\log_{10}A$ (s^{-1}) = 30.3

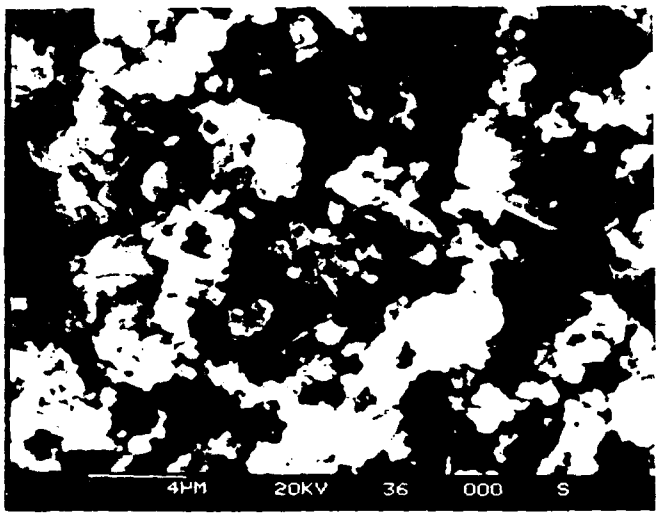
TABLE 5

Non-Isothermal DSC Characteristics for the Lower-Temperature Ignition Exotherm, "Q", associated with the Thermal Decomposition of BPBO (Boron: PbO, 10:90) (Ref 26)

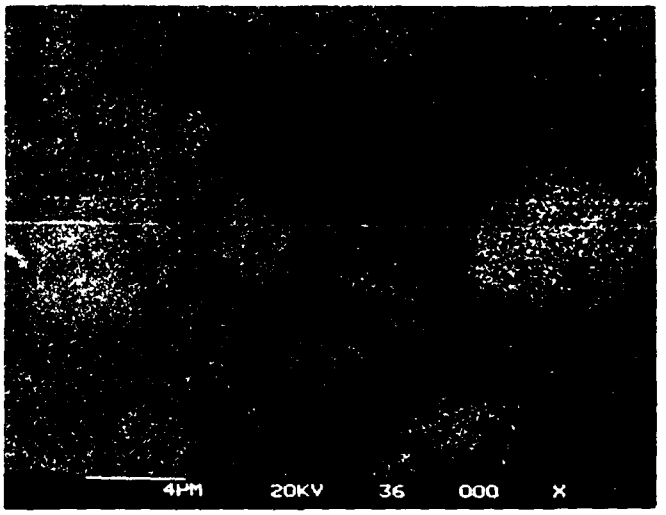
Heating Rate ($K\ min^{-1}$)	Mass (mg)	Exotherm (K)	
		T_{onset}	T_{max}
2.5	20.8	683	699
5	24.8	686	702
10	15.0	692	709
20	8.3	698	716
40	7.8	707	724

Kissinger Plot:

E^* ($kJ\ mole^{-1}$)	435.4
$\log_{10}A$ (s^{-1})	30.3
Correlation Coefficient	0.985



(a)



(b)

FIGURE 1 (a) Scanning electron micrograph of boron used in the formulation of BLC 190. Note the occasional large chunks of material in the mixture. These are from magnesium-containing impurities.

(b) Magnesium-specific x-ray probe of the boron sample above in almost the same configuration. The "cloudy patterns" correspond to the chunky Mg moieties quite conspicuous in Fig. 1(a).

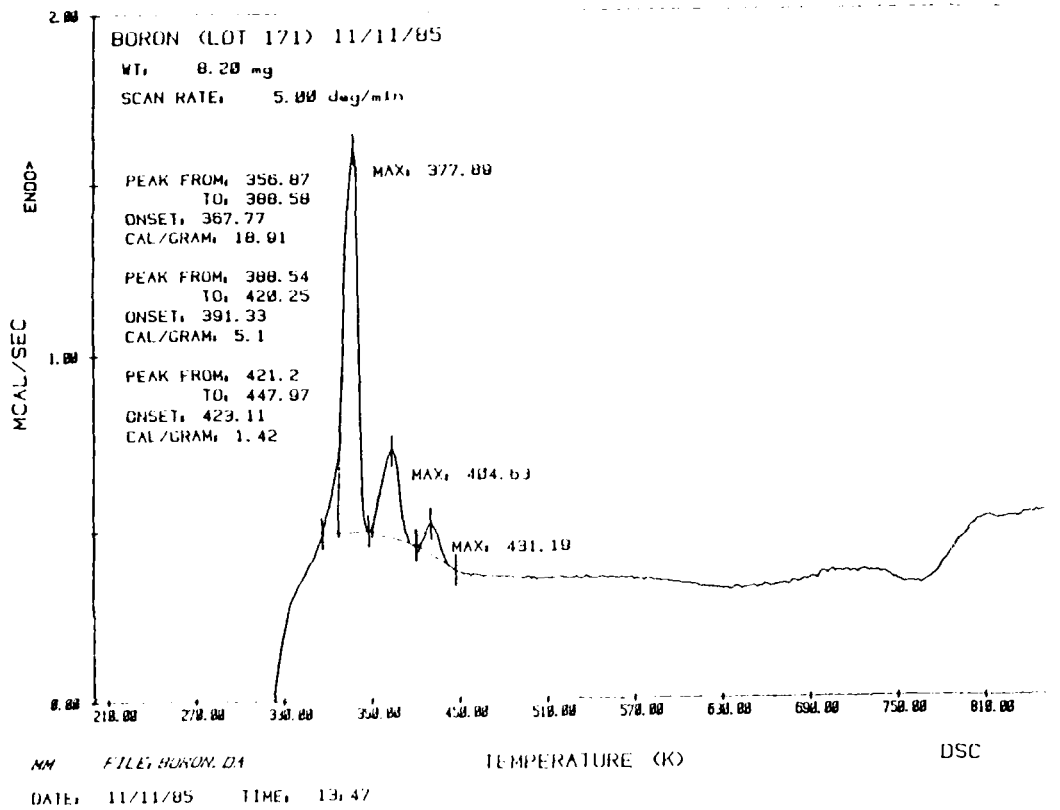


FIGURE 2 DSC trace of powdered boron (amorphous, washed, technical grade ex Trona) at a heating rate of 5 K min^{-1} in aluminium sample pans, under nitrogen.

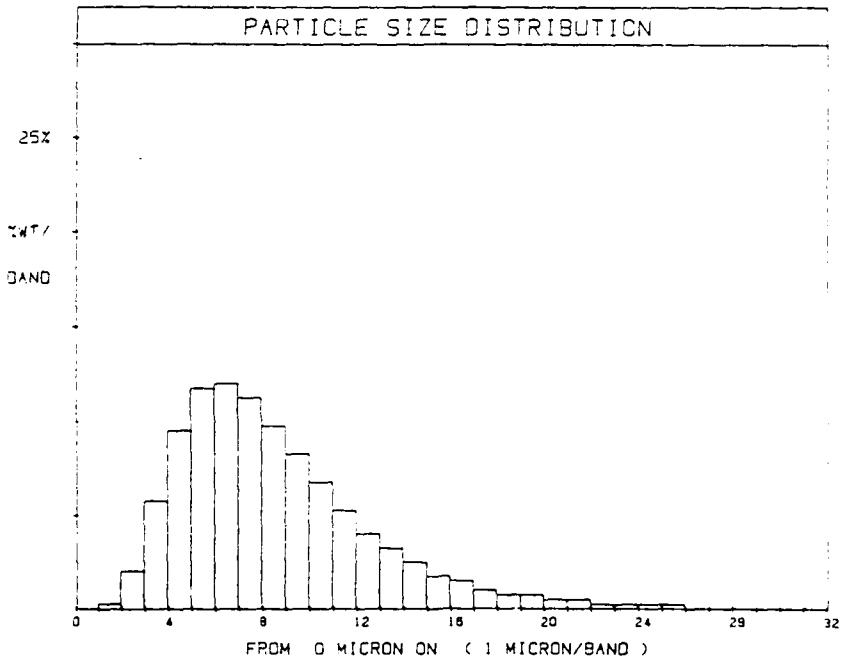


FIGURE 3 Histogram of the particle size distribution of red lead (ex May and Baker) as determined on the Malvern Particle Size Analyser.

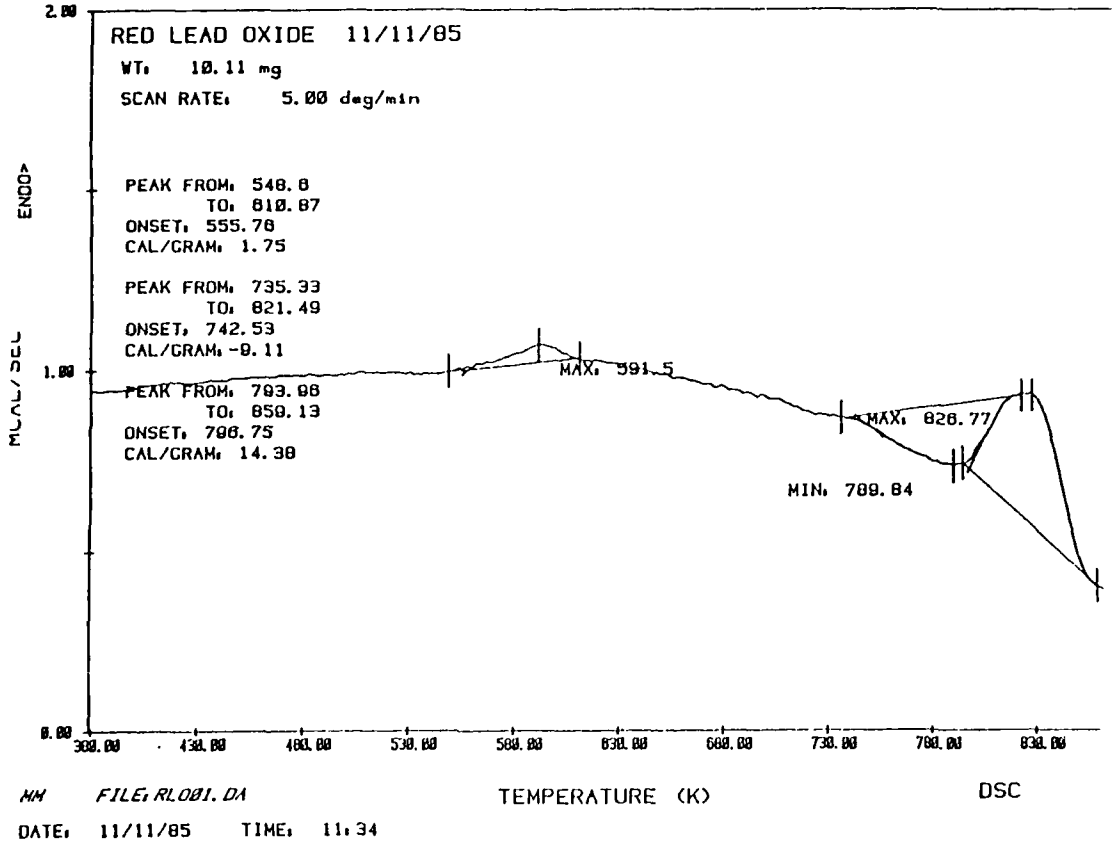


FIGURE 4 DSC trace of powdered Pb_3O_4 (ex May and Baker) at a heating rate of 5 K min^{-1} in aluminium sample pans, under nitrogen.

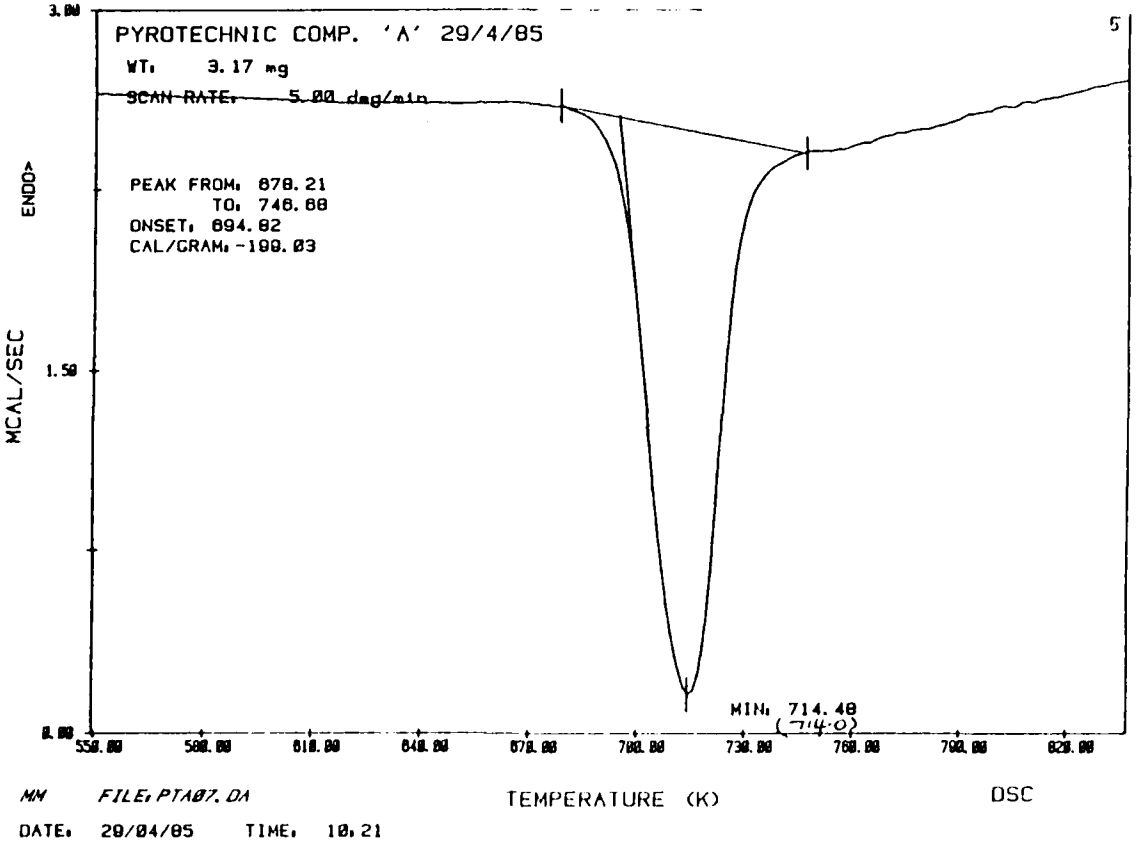


FIGURE 5 DSC trace of BLC 190 at a heating rate of 5 K min^{-1}, in aluminium sample pans under nitrogen.

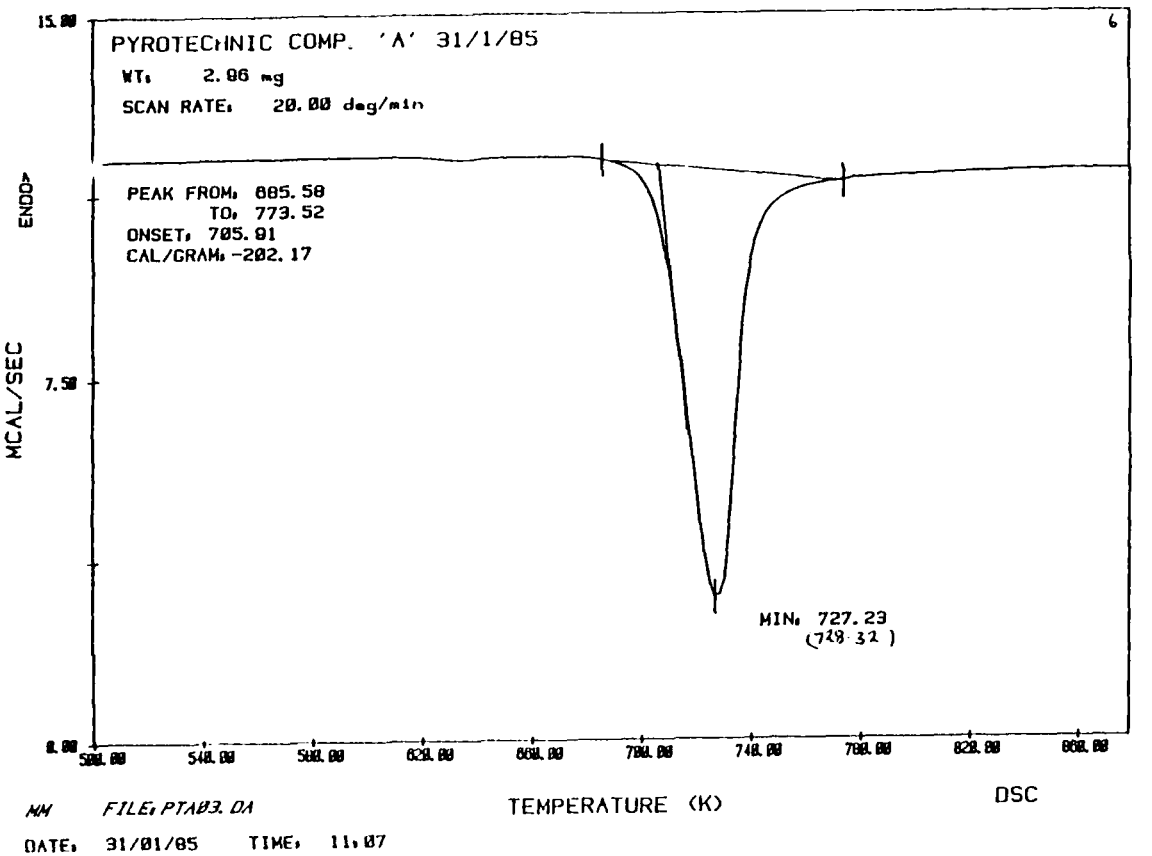


FIGURE 6 DSC trace of BLC 190 at a heating rate of 20 K min^{-1} in aluminium sample pans under nitrogen.

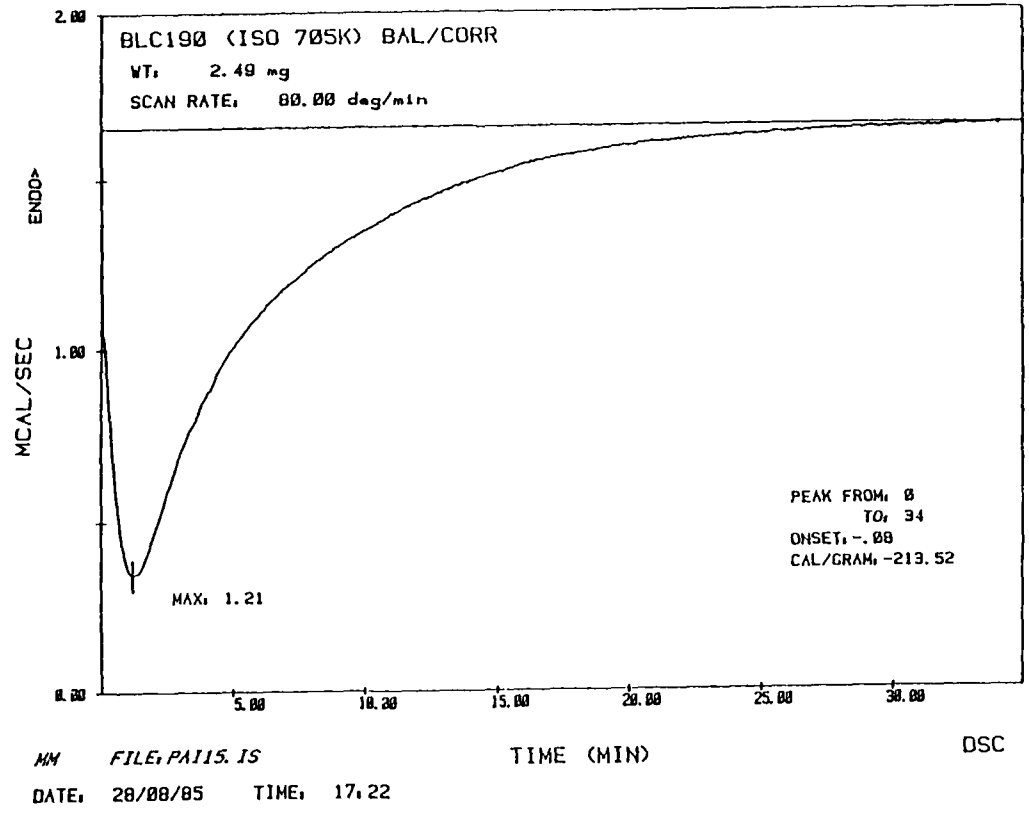


FIGURE 7 DSC trace of BLC 190 under isothermal conditions at 705 K, in an aluminium sample pan under nitrogen.

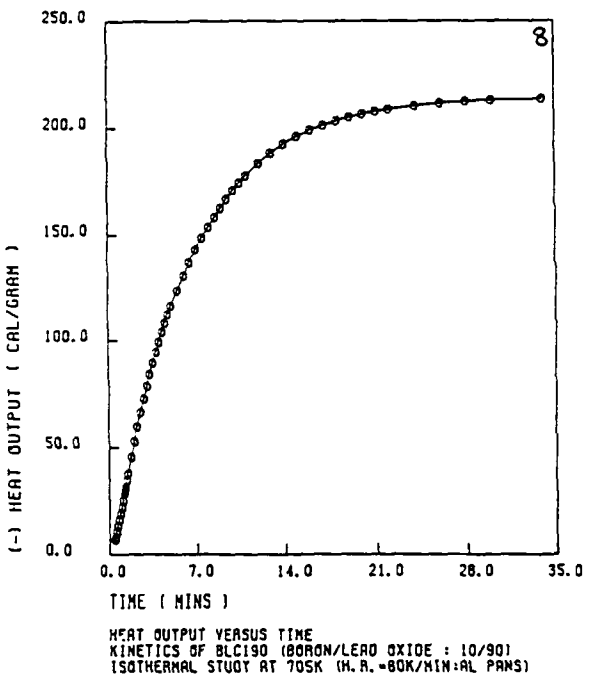


FIGURE 8 Heat output from BLC 190 under isothermal conditions at 705 K in an aluminium sample pan, under nitrogen.

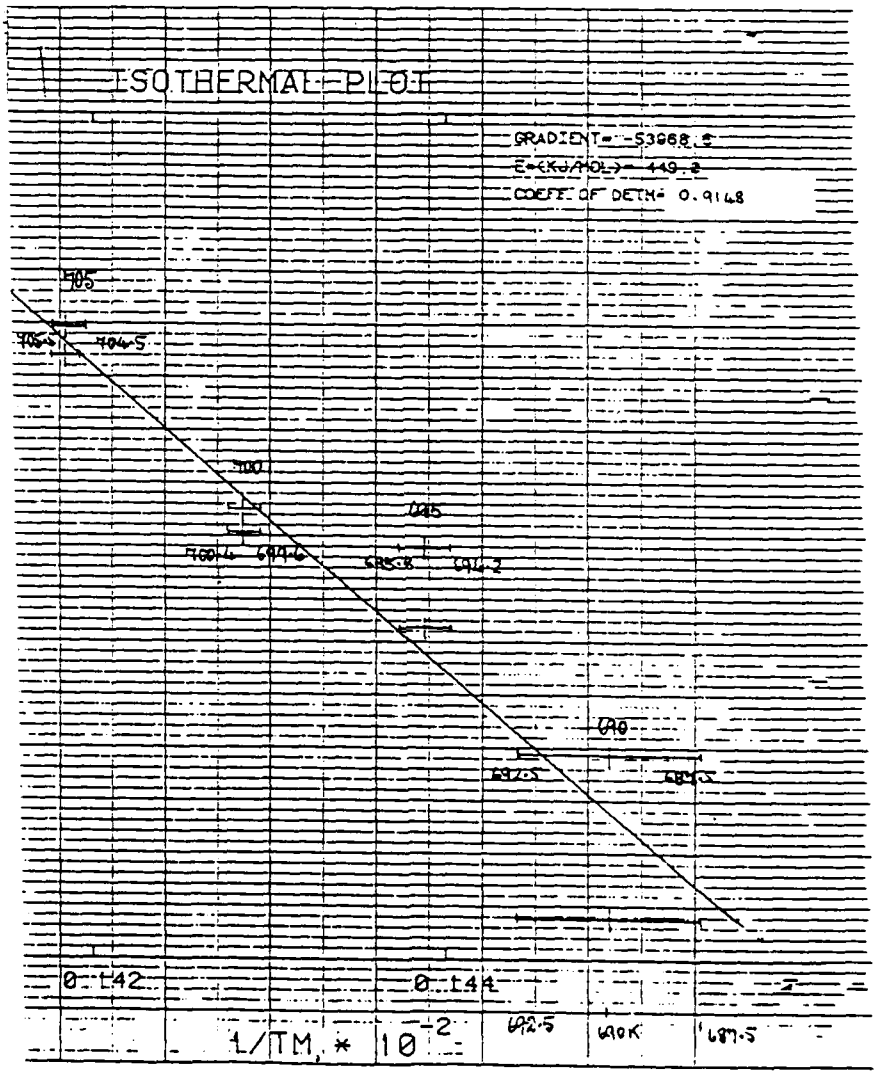


FIGURE 9 Arrhenius plot, ln k' vs. T^{-1}, for the thermal decomposition of BLC 190 in the temperature range 705 K - 690 K, (Table 3).

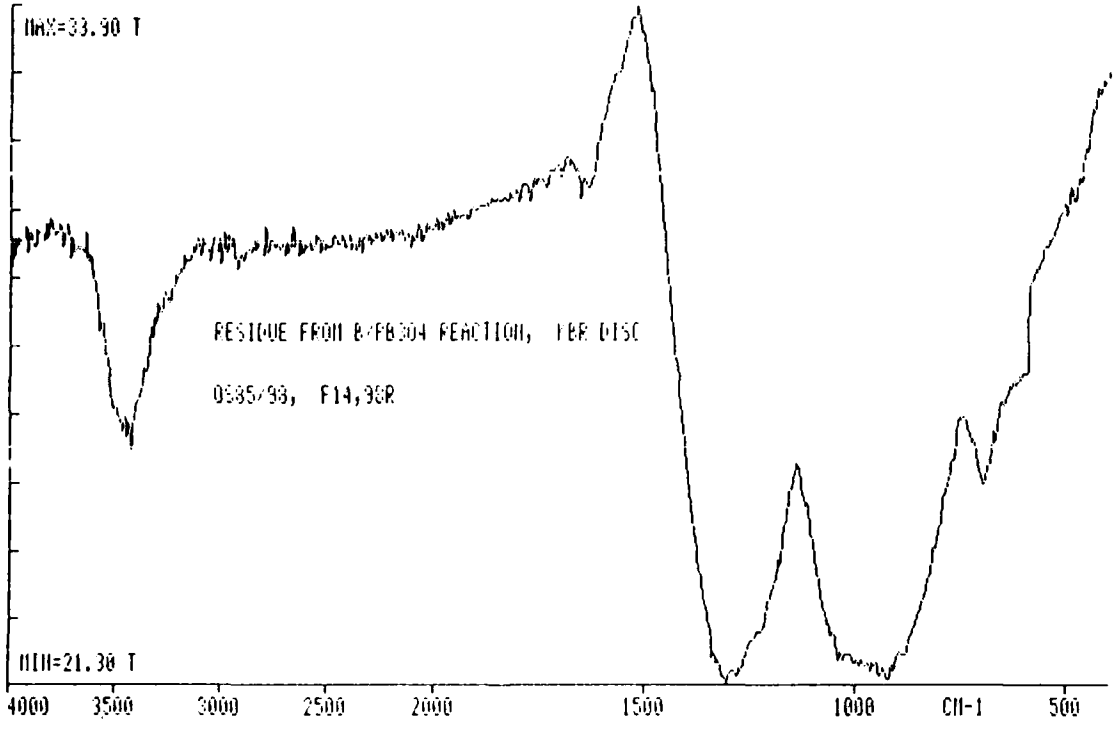


FIGURE 10 Infra red absorption spectrum (KBr disc) of the residue from the thermal decomposition of BLC 190 near 705 K.

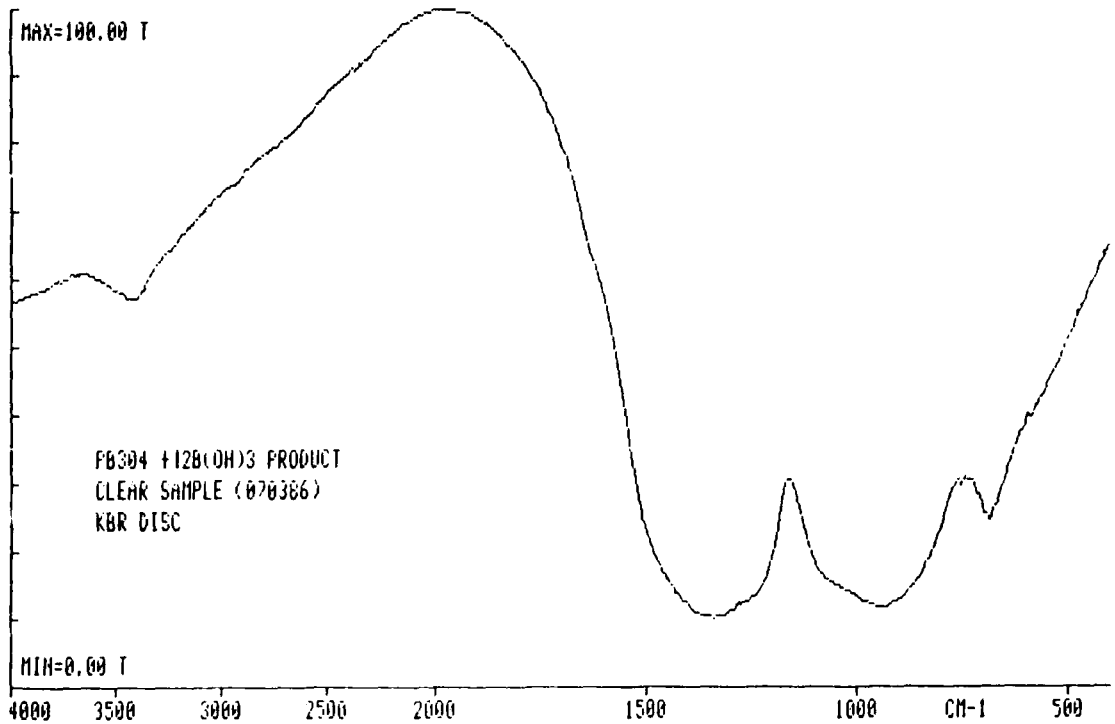


FIGURE 11 Infra red absorption spectrum (KBr disc) of lead tetraborate prepared from stoichiometric amounts of red lead, Pb_3O_4, and $B(OH)_3$ at 900^{o}-1000^{o} (Pt crucible).

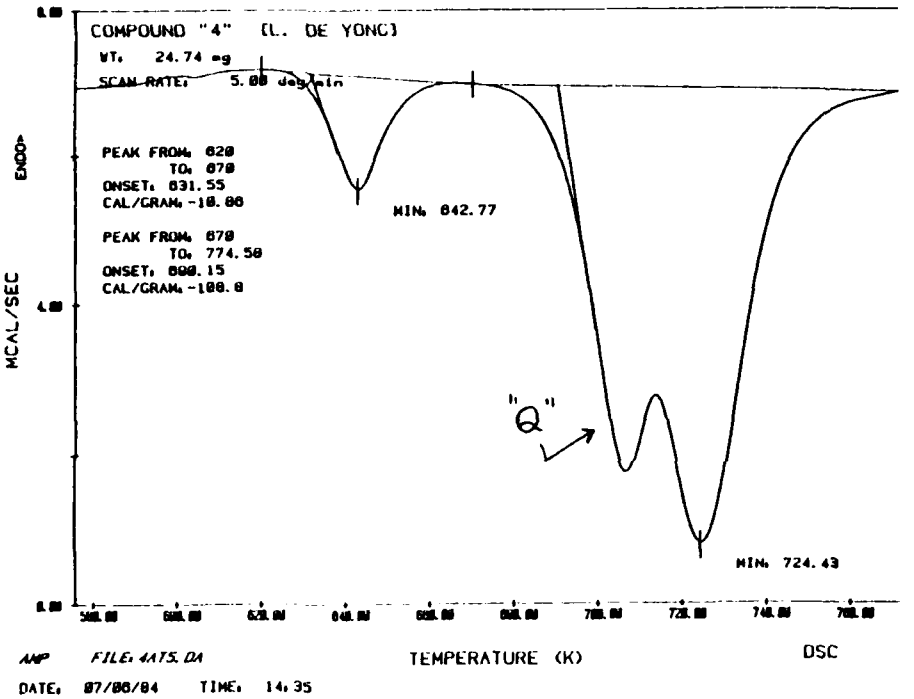


FIGURE 12 DSC trace of BPBO (boron:PbO, 10:90) at a heating rate of 5 K min^{-1} in an Al sample pan under nitrogen.

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REPORT

MRL-R-1037

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D.J. Whelan, M. Maksacheff
and L. de Yong

ABSTRACT

The thermal decomposition of the important pyrotechnic composition BLC 190 (boron:red lead, 10:90) has been studied by isothermal and non-isothermal differential scanning calorimetry (aluminium sample pans, nitrogen atmosphere). The decomposition has been found to proceed at temperatures around 700 K through a first-order reaction obeying a simple Arrhenius law with an activation energy 434 $kJ\,mol^{-1}$, pre-exponential $\log_{10}A\ (s^{-1}) = 29.7$ and heat of reaction 846 $J\,g^{-1}$.

No change in weight was observed in the reaction mixture, before and after heating and the end-product is a lead borate salt, $PbO.2B_2O_3$ or PbB_4O_7, rather than boric oxide. The reaction pathway appears to have a kinetic step similar to that of BPBO (boron: PbO, 10:90).

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